

# Coercivity Enhancement of HDDR Hot-Pressed Magnets by NdCu Diffusion Treatment

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In order to improve the coercivity of hot-pressed magnets with hydrogenation disproportionation desorption recombination (HDDR) powders being the precursor, diffusion processing of an NdCu eutectic alloy is employed for grain boundary modification, resulting in an increase of coercivity from 15.4 to 17.8 kOe, which leads to a better thermal stability with the temperature coefficient ( $\beta$ ) changing from  $-0.549\%/K$  to  $-0.519\%/K$ . It is evidently observed that Nd-rich grain boundary layers are formed between the adjacent matrix phase grains as well as in the junction parts after diffusion treatment, which is responsible for the coercivity enhancement of the HDDR hot-pressing magnets. The influence of the microstructure on the coercivity has been further investigated to reveal that the Nd-rich phases occurred during the boundary modification process of the NdCu eutectic alloy decouple the exchange interactions between the grains.

**Index Terms**—Coercivity, diffusion, hot pressing, hydrogenation disproportionation desorption recombination (HDDR).

## I. INTRODUCTION

THERE is an increasing demand for Dy-free high coercivity sintered magnets for the motors of hybrid electric vehicles. The coercivity at room temperature of the Nd-Fe-B magnets should be higher than 30 kOe for an operating temperature of  $\sim 200^\circ\text{C}$  [1]. One way to achieve this is the substitution of Dy for Nd, which increases the cost due to the scarcity of Dy. The other way for acquiring high coercivity is to refine the grain size of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase in the magnets. By means of reducing the grain size to  $1\ \mu\text{m}$ , Dy-free sintered magnets with coercivity of 19 kOe were prepared [2]. However, it is difficult to decrease the grain size to  $<1\ \mu\text{m}$  in the sintered magnets for higher coercivity at present.

The hydrogenation disproportionation desorption recombination (HDDR) process is an effective method to produce powders with an average grain size of 300 nm, equaling to the size of single magnetic domain for  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . This is a very useful technique for the production of high performance anisotropic bonded magnets or hot-pressing/deformed magnets [3], [4]. But, the coercivity of the HDDR magnets still remains not very high in spite of their finer submicrometer grain size. According to the previous report [5], this was attributed to the exchange coupling of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains caused by the lack of Nd-rich phase along the grain boundary. So, the modification of boundary layers becomes a key point to increase the coercivity of the HDDR magnets expected from magnetically isolated single domain particles. In this paper, the diffusion process of NdCu eutectic alloy into HDDR magnets

was used for Nd enrichment at the grain boundaries, which is beneficial for the coercivity enhancement. The relationship between the microstructures of the magnets and the coercivity has been discussed in detail.

## II. EXPERIMENT

Alloy ingots with nominal composition of  $\text{Nd}_{13.5}\text{Fe}_{\text{bal}}\text{Co}_{6.0}\text{Zr}_{0.1}\text{Al}_{1.5}\text{Ga}_{0.5}\text{B}_{6.5}$  were prepared by induction melting under an argon atmosphere. The ingots were homogenized at  $1120^\circ\text{C}$  for elimination of  $\alpha\text{-Fe}$  and pulverized into powders with a particle size of  $<150\ \mu\text{m}$ . For HDDR process, the powders of the alloy ingots were heated up to  $780^\circ\text{C}$ – $840^\circ\text{C}$  in a closed chamber with continuous hydrogen flow. After holding for 2–5 h with hydrogen pressure of 50 kPa, the DR process was carried on: hydrogen desorption under a pressure of 1–5 kPa for 1 h and recombination under a high vacuum of  $<3 \times 10^{-3}\ \text{Pa}$  for 0.5 h at the same temperature.

After the steps described previously, the HDDR-processed  $\text{Nd}_2\text{Fe}_{14}\text{B}$  powders were used to prepare hot-pressing magnets. First, a cylinder of green compact was obtained under an alignment field of 2 T perpendicular to the pressing direction and then isostatically processed at a 160 MPa pressure. After that the as-got compact was put into an alloyed die followed by hot pressing at  $740^\circ\text{C}$  under 270 MPa in vacuum with a processing time of 5 min. This alloyed die is made from tungsten steel with an inner diameter of 10 mm. The hot-pressing direction was parallel to the cylinder axis which is perpendicular to the initial pressing direction and parallel to the alignment direction. Bulk hot-pressed sample of  $\Phi 10\ \text{mm} \times 12\ \text{mm}$  was acquired and its density was  $7.54\ \text{g/cm}^3$ . The  $\text{Nd}_{70}\text{Cu}_{30}$  alloy was prepared by induction melting and crushed into powders with the size of  $\sim 50\ \mu\text{m}$ . Then, the hot-pressed magnets were cut into pieces of  $\Phi 10\ \text{mm} \times 1\ \text{mm}$  and were soaked into  $\text{Nd}_{70}\text{Cu}_{30}$  alloy

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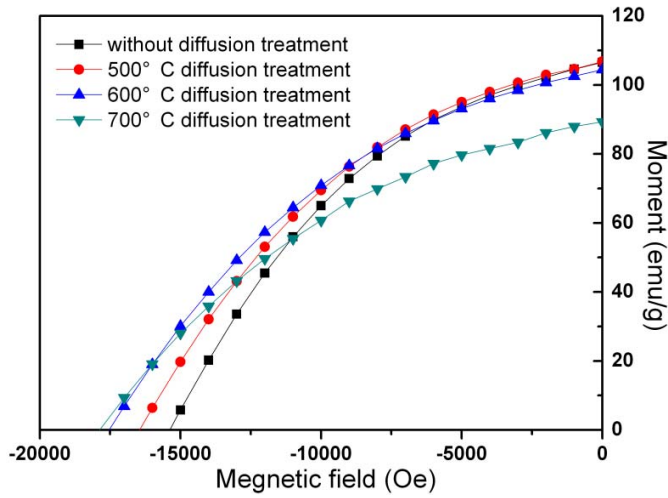


Fig. 1. Demagnetization curves of the initial and diffusion treated HDDR magnets with different processing temperatures.

powders and treated at temperatures of 500 °C, 600 °C and 700 °C, respectively. After diffusion treatment, small cylinders of  $\Phi 3 \text{ mm} \times 1 \text{ mm}$  were prepared for magnetic measurements. The coercivity of the initial and diffusion-processed magnets was measured by magnetic properties measurement system. The microstructures were investigated by back scattering electron (BSE) scanning electron microscopy (SEM). High-resolution transmission electron microscopy (HR/TEM) was utilized to make observations of the detailed microstructure of the magnets.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the demagnetization curves of the initial and NdCu alloy diffused HDDR hot-pressing magnets with different processing temperatures of 500 °C, 600 °C and 700 °C, respectively. The coercivity of the magnet without diffusion treatment is 15.4 kOe and gradually increases to 16.4, 17.5, and 17.8 kOe with the increase of diffusion temperatures. The remanent magnetization of the magnets diminishes unremarkably when processed at 600 °C while an apparent reduction of remanence occurred at a higher diffusion temperature of 700 °C. The influence of the microstructure on the coercivity as well as the remanent magnetization is analyzed further in the following paragraph.

Fig. 2 shows the coercivity versus temperature plots of the initial and the 700 °C diffusion treated HDDR magnets. The temperature coefficient ( $\beta$ ) of the coercivity for the two samples is  $-0.549\%/K$  and  $-0.519\%/K$ , indicating an improvement of  $\beta$  during diffusion process. It is relatively comparable with the typical value for commercial NdFeB sintered magnets with a temperature coefficient of about  $-0.6\%/K$  [6].

The BSE SEM images of the initial, 600 °C and 700 °C diffusion treated HDDR hot-pressed magnets are shown in Fig. 3. There is no distinct bright contrast between the grain boundary layers and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains in most parts within the initial magnet except for the regions close to the agglomeration of Nd-rich phase [Fig. 3(d)]. This agglomeration originates from the microstructure of the starting alloy before HDDR

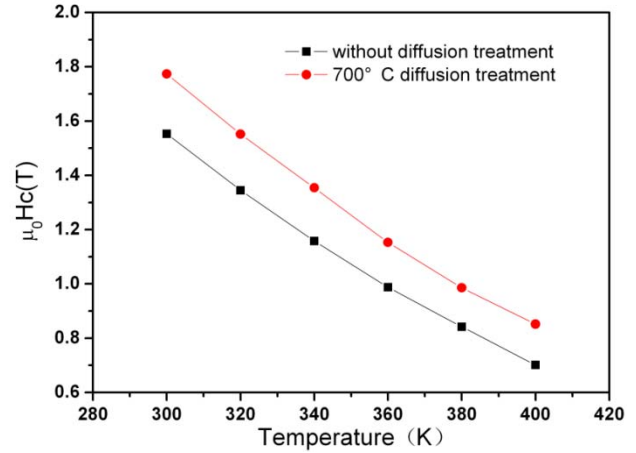


Fig. 2. Coercivity versus temperature plots of the initial and 700 °C diffusion treated HDDR magnets.

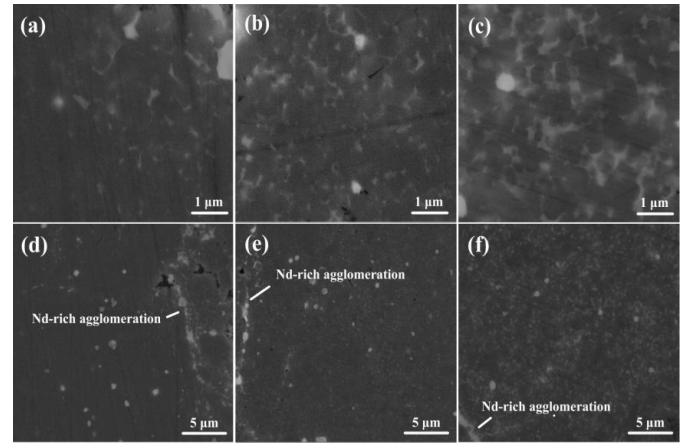


Fig. 3. BSE SEM images of the initial (a,d), 600 °C (b,e) and 700 °C (c,f) diffusion treated HDDR magnets.

processing progress. The Nd-rich phase here was considered as the Nd source for the development of the grain boundary phase of the HDDR powders, which generated mobile Nd-rich liquid during DR step [7]. So, only the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains near the agglomeration regions [Fig. 3(a)] are enclosed by the Nd enriched phases without NdCu diffusion treatment, which leads to relatively low coercivity. After the diffusion processing of NdCu eutectic alloy into the HDDR hot-pressing magnet at 600 °C and 700 °C, the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains are separated uniformly by the Nd-rich phases as observed in Fig. 3(b) and (c), both in the agglomeration and other regions [Fig. 3(e) and (f)]. The coercivity improvement from 15.4 to 17.8 kOe probably stems from enhanced pinning effect of the boundary layer between the matrix phase grains owing to the Nd enriched boundary phases [8]. It should be noticed that the fraction of Nd-rich phase area in 700 °C diffused magnet is significantly larger than that of the 600 °C diffused one which presents less Nd-rich phases at  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grain junctions in most parts of the magnets. This is considered to be the contribution to significant decrease on the remanent magnetization between 600 °C and 700 °C diffused magnets.

Fig. 4(a) and (b) shows TEM images of the initial and 700 °C diffusion processed HDDR hot-pressed magnets, respectively. The average size of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains was

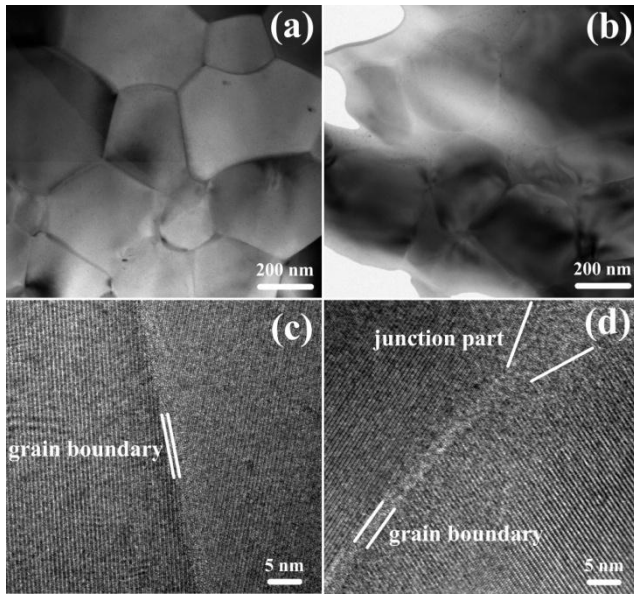


Fig. 4. TEM/HRTEM images of the initial (a,c) and 700 °C diffusion treated (b,d) HDDR magnets.

both from 230 to 550 nm, indicating no distinct grain size growth during the diffusion process. Without diffusion, the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains are connected directly with the neighboring ones due to the lack of Nd-rich phase, which was ascribed to the agglomeration of the Nd enriched region occurred in the HDDR processing. Fig. 4(c) shows the HRTEM image of the corresponding Fig. 4(a), demonstrating that extremely thin grain boundary layer existed before the NdCu alloy diffusion treatment, resulting in some exchange coupling between neighboring grains, which limits the coercivity. The grain boundary layer seems to be amorphous with a thickness of nearly 1 nm, which was similar to sintered magnets according to a previous report [9]. Besides, such thin layer may not be adequate to reduce or remove defects at the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grain interface. When the 700 °C diffusion process was applied to the HDDR hot-pressed magnets, distinct and thick Nd-rich grain boundary phases formed as well as plenty of Nd enriched phases in the junction parts of adjacent grains. The thickness of the boundary layers reached 2–3 nm smoothly to decouple the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains with respect to magnetic exchange interaction and therefore increase the coercivity of the processed HDDR hot-pressed magnet. According to the expression of the ferromagnetic exchange coupling length ( $L_{\text{ex}}$ ) in hard magnetic materials, i.e.,  $L_{\text{ex}} = (A/K)^{1/2}$ , where  $A$  is the exchange stiffness and  $K$  is the anisotropy constant, the ferromagnetic exchange length ( $L_{\text{ex}}$ ) of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  of 1.3 nm and the domain wall width ( $\pi L_{\text{ex}}$ ) of 4.1 nm can be given by introducing the intrinsic magnetic parameters ( $A = 7.7 \times 10^{-12} \text{ Jm}^{-1}$ ,  $K = 4.3 \text{ MJm}^{-1}$ ) of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  [9]. A thickness of the grain boundary between the two values may either decouple the exchange interactions or pin the magnetic domain walls to improve the coercivity. The junction part, also making a contribution to the coercivity enhancement [10], showed amorphous characteristic at the interface to the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  grains, which is regarded different to that in the case of crystalline Nd-rich phase present between the grains for sintered magnets.

The influence of the amorphous phases in the junction parts has not been well investigated in such kind of magnets.

#### IV. CONCLUSION

The coercivity of the HDDR hot-pressed NdFeB magnets can be improved from 15.4 to 17.8 kOe by means of diffusion treatment of an NdCu eutectic alloy. The influence of the microstructures of such magnets on the coercivity has been investigated. As a result, the Nd-rich grain boundary phase plays an important role not only by enhancing the pinning effect, but also by decoupling of the exchange interactions between the neighboring grains. Further optimization of the microstructures will be continued for better magnetic properties of HDDR magnets in the future.

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